

AD-A087 364

TEXAS UNIV AT AUSTIN DEPT OF CHEMISTRY F/G 7/4  
PHOTOCATALYTIC PRODUCTION OF HYDROGEN FROM WATER AND TEXAS LIGN--ETC(U)  
JUL 80 S SATO, J M WHITE N00014-75-C-0922

NL

UNCLASSIFIED

141  
S.A.:



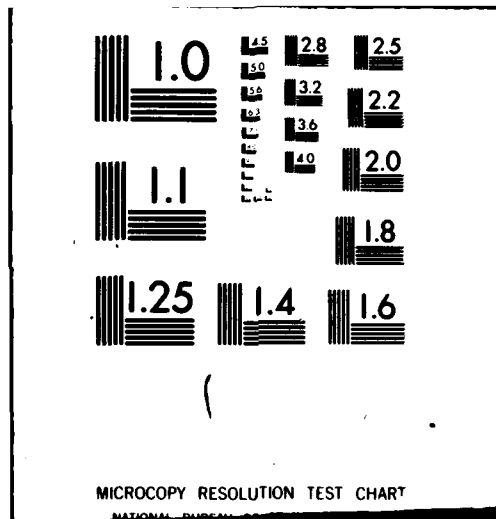
END

DATE

FILED

9-80

DTIC



ADA 087364

LEVEL

12

OFFICE OF NAVAL RESEARCH

Contract No. N00014-75-C-0922

Task No. NR 056-578

Technical Report No. 16

Photocatalytic Production of Hydrogen from Water  
and Texas Lignite using a Platinized Titania Catalyst

by

Shinri Sato and John M. White

Prepared for Publication

in

I&EC Product Research and Development

Department of Chemistry

University of Texas at Austin

Austin, Texas 78712

July 15, 1980

347 83  
DTIC  
ELECTE  
AUG 1 1980  
S D  
A

Reproduction in whole or in part is permitted  
for any purpose of the United States Government  
Approved for Public Release; Distribution Unlimited

THIS DOCUMENT IS BEST QUALITY PRACTICABLE.  
THE COPY FURNISHED TO DDC CONTAINED A  
SIGNIFICANT NUMBER OF PAGES WHICH DO NOT  
REPRODUCE LEGIBLY.

DDC FILE COPY

80 7 30 020

## **DISCLAIMER NOTICE**

**THIS DOCUMENT IS BEST QUALITY  
PRACTICABLE. THE COPY FURNISHED  
TO DTIC CONTAINED A SIGNIFICANT  
NUMBER OF PAGES WHICH DO NOT  
REPRODUCE LEGIBLY.**

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD A08 7364	(9)
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
(6) Photocatalytic Production of Hydrogen from water and Texas Lignite using a Platinized Titania Catalyst.		Technical Report, no 16, Jan 1980-Dec 1980
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)
(10) Shinri Sato and John M. White		(15) N00014-75-C-0922 (31)
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
J.M. White, Department of Chemistry University of Texas at Austin Austin, Texas 78712		Project NR 056-578
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Department of the Navy Office of Naval Research Arlington, Virginia 22217		(11) 15 Jul 1980
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
(12) 11		16
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for Public Release: Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
Preprint, accepted, American Chemical Society		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Using a physical mixture of powdered Texas lignite and platinized titania in the presence of water vapor and ultraviolet light, we show that a catalytic reaction occurs at 23°C to form hydrogen and carbon dioxide. These results are contrasted with a recent electrochemical conversion process.</p>		

Photocatalytic Production of Hydrogen from Water  
and Texas Lignite using a Platinized Titania Catalyst (a)

Shinri Sato and John M. Whites

Department of Chemistry  
University of Texas  
Austin, Texas 78712

Abstract

Using a physical mixture of powdered Texas lignite and platinized titania in the presence of water vapor and ultraviolet light, we show that a catalytic reaction occurs at 23°C to form hydrogen and carbon dioxide. These results are contrasted with a recent electrochemical conversion process.

(a) Supported in part by the Office of Naval Research.

Accession For	
5000 G-441	<input checked="" type="checkbox"/>
500 115	<input type="checkbox"/>
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	23 Q

1. Introduction.

The conversion of solar energy into chemical energy is a topic of considerable current interest particularly as it has an impact on fuel production and conversion utilizing readily available raw materials. Considerable work has been done on the photo-driven decomposition of water and the notable success of photoelectrochemical cells in achieving this end has recently been reviewed (Marusak and Ghosh, 1978). We have recently reported a photocatalytic system, illuminated platinized titania, which functions at 23°C and in the absence of external potentials, as an ordinary heterogeneous catalyst for the reactions of gaseous water with hydrocarbons, active carbon and carbon monoxide (Sato and White, 1980 a,b). A similar system, using gas or liquid phase water,  $\text{RuO}_2/\text{TiO}_2$ , and light, has also been reported (Kawai and Sakata, 1979a,b). These results extend the interesting work on liquid phase photocatalytic reactions that has been reviewed (Bard, 1979). For example, using platinized titania, liquid phase acetic acid can be converted to methane (Kraeutler and Bard, 1978a). A general review of heterogeneous photocatalysis has also appeared recently (Formenti and Teicher, 1979).

As compared to photoelectrochemical systems, heterogeneous catalyst systems do offer several advantages: (1) they are generally simpler to construct and are less expensive, (2) a wider variety of materials in different forms can be used, (3) because of diffuse light scattering by powders, more efficient light utilization can be achieved, (4) the reactants can be in the gas, liquid or solid

phase and (3) a wider range of temperatures are feasible when using gas and/or solid phase reactants. Because of these advantages, heterogeneous photocatalytic systems deserve attention as potential solar-to-chemical energy converters.

Such systems would be helpful in the utilization of lignites. Many processes have been and are under study. For example, an interesting electrochemical process which converts coal and water into hydrogen and carbon oxides, mainly  $\text{CO}_2$  has recently been reported (Coughlin and Farooque, 1979). This system operates at electrical potentials significantly lower than the thermodynamic potential of water electrolysis because the oxidation of carbon is claimed. Moreover, they found that lignite and char are more easily oxidized anodically than parent coals. We report here another process producing hydrogen and carbon dioxide from lignite and water vapor in which light, but no electrical power, is used.

## 11. Experimental.

$\text{TiO}_2$  (anatase) was obtained from HCB, pretreated for 6 hr at  $700^\circ\text{C}$  in flowing  $\text{H}_2$ , cooled in hydrogen and stored in a sample vial. Samples of this material were platinumized (2 wt. % Pt) by the photolysis at  $55^\circ\text{C}$  of a hexachloroplatinic acid solution containing suspended  $\text{TiO}_2$  powder (Krausler and Bard, 1978b). After photolysis the sample was washed with distilled water until  $\text{Cl}^-$  could not be detected. It was then dried in a desiccator until used. The BET surface area, determined using  $\text{N}_2$ , was  $11 \text{ m}^2 \text{ g}^{-1}$ .

Texas lignite, containing 64% C, 17% O, 5% H, 1% N, 0.1% S and small amounts of metals, (Edgar, 1979) was ground in a mortar (estimated average particle size  $\approx 100 \mu\text{m}$ ) and physically mixed (20 wt.%) with the catalyst. A 0.25 gm sample of this mixture was spread uniformly on the bottom flat window of a quartz reaction cell and connected into an evacuable, closed circulation system ( $180 \text{ cm}^3$ ). This assembly was linked to a mass spectrometer for product analysis. Distilled water, outgassed several times at dry ice temperature, was stored in a tube on the vacuum line.

After outgassing the sample for 3 hrs. at  $200^\circ\text{C}$ , it was cooled to  $23^\circ\text{C}$  and approximately 24 torr of water was added. This system was illuminated with a 200w high pressure mercury arc that was filtered through a  $\text{H}_2\text{SO}_4$  solution to remove most of the infrared light. Small aliquots of the gas phase were taken at various times and, after passage through a cold trap (about  $-110^\circ\text{C}$ ) to remove water, were analyzed with the mass spectrometer.

Figure 1 shows a typical time evolution of products. The rate of hydrogen production over the first twenty minutes is about  $2 \times 10^{-2}$  torr min<sup>-1</sup> but this drops to a nearly constant value of  $9 \times 10^{-3}$  torr min<sup>-1</sup> over the subsequent eighty minutes. The other major product was CO<sub>2</sub> and over the time interval 20-100 min, the ratio H<sub>2</sub>/CO<sub>2</sub> drops slowly from 2.75 to 2.55. Minor amounts of O<sub>2</sub> and CH<sub>4</sub> were also found; after 100 min,  $P_{O_2} = 10^{-3}$  torr and  $P_{CH_4} = 6 \times 10^{-3}$  torr. No other products were detected, in particular H<sub>2</sub>S was not produced from sulfur impurities in the lignite. The hydrogen formation rate and its time dependence compares favorably with that observed in the active carbon reaction. For example, at 100 min. the H<sub>2</sub> rate in the active carbon reaction is  $7 \times 10^{-3}$  torr min<sup>-1</sup>. However, no oxygen was detected and the H<sub>2</sub>/CO ratio was very nearly 2 in the latter (Sato and White, 1980). Here the ratio is greater than two probably because hydrogen in the lignite is partly converted to H<sub>2</sub>.

Significantly, the catalyst only slowly lost its activity during repeated runs involving system evacuation followed by restoration of the water pressure. Irradiation of Pt/TiO<sub>2</sub> in the absence of lignite produced limited amounts of H<sub>2</sub> ( $< 10^{-1}$  torr) over extended periods. This was accompanied by even smaller amounts of CO<sub>2</sub> but no oxygen was observed. These products are thought to arise from the oxidation of residual carbon on the catalyst. It is also of interest to consider whether the observed H<sub>2</sub> could arise from the non-catalytic reaction of surface hydroxyl groups present on the TiO<sub>2</sub>. According to the literature (Boonstra and Mutsaers, 1975) the number of OH groups on both anatase and rutile declines with increasing outgassing temperature. Based on their results, we estimate a surface hydroxide concentration of less than  $2 \times 10^{18}$  m<sup>-2</sup>.

If all these were converted to hydrogen then we would expect to produce less than 0.5 torr of H<sub>2</sub>. Figure 1 shows that 1.2 torr of hydrogen is produced in 110 min with no evidence of a rapidly declining rate. Moreover, eight hours of production time (see below) involved in Fig. 2 and the rate is never less than  $0.75 \times 10^{-2}$  torr min<sup>-1</sup>. The total H<sub>2</sub> production over this period is thus greater than 3.6 torr. From these results we conclude that surface hydroxide initially present on these TiO<sub>2</sub> samples can not account for the observed amounts of hydrogen.

Figure 2 shows the H<sub>2</sub> formation rate and the O<sub>2</sub> pressure as a function of reaction time for six consecutive experiments involving the same catalyst/lignite sample. Between each experiment, the system was evacuated, treated in some way and the water pressure restored. Prior to experiments (1) and (4) the sample was created by outgassing for 3 hr at 200°C. Prior to the other four experiments the sample was outgassed at 23°C for 10 min. The dotted line in Fig. 2 connects the initial rates for the six experiments and shows that the activity declines with use and is not fully reactivated by outgassing at either 23 or 200°C. During the course of a single run the activity drops rapidly over the first twenty minutes and then declines much more slowly (as in Fig. 1). This trend is followed in each of the six experiments. After one hour into experiment 5, the temperature was raised from 23 to 60°C. This gave no increase in rate over a time interval of 30 min.

In the lower part of Fig. 2, the O<sub>2</sub> pressure as a function of time is shown for each experiment. In general these results show (1) that the oxygen accumulation rate increases with the number



of experiments that involve outgassing at 23°C. (2) that outgassing at 200°C reduces the subsequent oxygen production rate, (3) that oxygen accumulation is limited and in some cases goes through a maximum and (4) that increasing the temperature accelerates the rate of oxygen removal.

#### IV. Discussion.

The data shown in Figs. 1 and 2 clearly demonstrate the photocatalytic reaction of water and lignite to produce hydrogen and carbon dioxide. The thermodynamics of this process are not known since the lignite is not well-characterized chemically. Based on the thermodynamics of solid carbon, ethane, ethylene and other small C<sub>n</sub>H<sub>m</sub> molecules we expect  $\Delta G^\circ > 0$ . Thus, through the use of light we have successfully driven this thermally uphill reaction and have done so in a catalytic sense.

The quantum efficiency, although it could be improved with a different cell design, is not high. Assuming an upper limit of  $10^{17}$  photons sec<sup>-1</sup> irradiate the catalyst, based on H<sub>2</sub> actinometry and thermopile measurements (White, 1966) then the H<sub>2</sub> production rate of  $9 \times 10^{-3}$  torr min<sup>-1</sup> corresponds to a quantum yield of 0.01. The energy efficiency, that is the net increase in energy stored per unit of light energy input, is estimated as 0.0003 assuming conservatively that the free energy decrease per mole of H<sub>2</sub> formed is 10 kJ mole<sup>-1</sup>. This calculation is based on the conversion of olefinic material (Sato and White, 1980).

The results reported here can be compared qualitatively with electrochemical conversions (Coughlin and Paroquet, 1979). These authors observed a gradual decrease of the reaction rate in their coal-water process which they ascribed to the accumulation of surface functional groups, such as carboxyl groups, on coal. They also found that the initial high anodic current could be regained if the coal was removed from the electrolyte (after the current had decreased to low value), heated to about 200°C, and then returned

to the system. In our process, however, an outgassing treatment of the sample at 200°C had no effect on the reaction rate (see Run 4 in Fig. 2). The temperature dependence of the  $H_2$  production was also slight as seen from the last part of Run 5 in Fig. 2. The apparent activation energy in the electrochemical experiments was 40-48 kJ mole<sup>-1</sup> and that in the  $RuO_2/TiO_2$  system was also significant (Kawai and Sakata, 1979). In a separate experiment we outgassed a sample at 60°C and then measured the reaction rate at 60°C. The rate was somewhat less than observed at 23°C.

The  $O_2$  data are very interesting because they indicate that the Pt is covered by some species which inhibits (poisons) the reaction of  $O_2$  and  $H_2$  on Pt. In the absence of poisoning the back reaction with oxygen is far faster than the  $O_2$  formation rate (Sato and White, 1979a). These results are distinct from those on active carbon (Sato and White, 1979b) where no  $O_2$  was observed. Perhaps sulfur accumulates at Pt as the reaction proceeds and allows the accumulation of oxygen. Heating to 200°C may cause the migration or desorption of this sulfur-containing species and subsequently the clean Pt serves to suppress  $O_2$  formation.

The mechanism of the reaction can not be established from the data reported here. However, our other work (Sato and White, 1979) makes it clear that band gap radiation is involved so we conclude, as expected, that the incident photons activate the catalyst by forming electron-hole pairs near the surface. Due to band bending, the hole will stay at (or migrate to) the surface while the electron will move away from the surface and eventually arrive at a neighboring Pt particle. One possible product formation mechanism involves the inter-

action of water with holes at  $TiO_2$  sites to form  $O(e^-)$  and/or  $OH(e^-)$  with concomitant formation of  $H^+$  which moves to a neighboring Pt site where it picks up an electron and is recombined to form  $H_2$ . The active oxygen species are used to oxidize carbon which is in contact with the catalyst; the products expected are  $CO_2$  and  $H_2O$ .

A mechanism involving desorbed gas phase  $O_2$  reacting with ligite can be ruled out because  $CO_2$  production was very slow in systems where the catalyst/ligite mixture was illuminated in the presence of  $O_2$ . An additional comment on the mechanism can be made on the basis of the following experiment. The addition of 0.3 torr of  $^{13}CO$  to the catalyst/ligite/water system reduced the rate of  $H_2$  production by about a factor of 2 and the water-gas shift reaction took place at about 20% of the rate of  $H_2$  production. This result indicates an inhibitory effect of CO probably because  $H_2$  recombination on Pt is retarded by adsorbed CO. During this experiment there was no significant dilution of  $^{13}CO$  with  $^{12}CO$  (i.e. insignificant isotope exchange) and no  $O_2$  was formed.

The relatively rapid decrease of the  $H_2$  production rate at the beginning of a reaction is not understood. Perhaps as  $H_2$  accumulates, back reactions with oxygen species formed on  $TiO_2$  become relatively more important. Other possibilities include inhibitory effects of traces of CO formed in the reaction or the loss of excellent contact between ligite and catalyst particles. Interestingly, the  $H_2$  formation does increase with the ligite/catalyst ratio; a 20% increase was noted when the weight ratio was doubled from 0.1 to 0.2. This observation points to the real

possibility of substantially improving the efficiency. Because of its importance as a fuel, the formation of  $\text{CH}_4$  ( $6 \times 10^{-3}$  torr at 100 min, Fig. 1) is of interest in spite of the fact that the yield is small. Repeated experiments, as in Fig. 2, were characterized by a rapid decrease in the rate of  $\text{CH}_4$  production. Moreover, these rates were not affected by the addition of  $\text{CO}_2$  (55 torr) to the system thus eliminating the possibility that  $\text{CH}_4$  arises from hydrogenation of  $\text{CO}_2$ . One possible mechanism involves the contact of ligate particles with Pt sites where hydrogenation can occur. If this conjecture has any merit, then the rate of  $\text{CH}_4$  formation could be improved by modifying the catalyst-ligate contact.

#### V. Summary and Conclusions.

The results of these experiments demonstrate that lignite coal and gas phase water can be catalytically converted to  $\text{CO}_2$  and  $\text{H}_2$  over a  $\text{Pt/TiO}_2$  catalyst illuminated with band-gap light. Significantly, the reaction occurs readily at 23°C. The quantum efficiency is only about 0.01 but can be significantly improved through the use of a different reactor design and through changes in the ligate/catalyst ratio.

The success of these experiments, coupled with the electrochemical results (Coughlin and Paroquet, 1979) which demonstrate hydrogen production rates at oxidation potentials well below one volt, suggests that narrower band gap semiconductors that are doped with transition metals offer some promise as catalysts for the gasification of lignite. Hopefully, by using gaseous water some of the semiconductor decomposition and oxidation problems encountered in photoelectrochemical cells can be avoided.

#### Acknowledgment

We thank Professor T. F. Edgar for furnishing the Texas lignite sample.

# References

- Kraeutler, B. and Bard, A. J., *J. Am. Chem. Soc.* **100**, 2239 (1978a).  
 Kraeutler, B. and Bard, A. J., *J. Am. Chem. Soc.* **100**, 4317 (1978b).  
 Bard, A. J., *J. Photochem.* **10**, 59 (1979).  
 Bonstra, A. M. and Nuttner, C.A.H.A. *J. Phys. Chem.* **79**, 1694 (1975).  
 Coughlin, R. W. and Farooque, M., *Nature* **279**, 301 (1979).  
 Edgar, T. F. (1979), University of Texas at Austin, private communication.  
 Forciniti, M. and Teichner, S. J. in Specialist Periodical Reports-Catalysis **2**, 87 (1979).  
 Kawai, T. and Sakata, T., *J.C.S. Chem. Comm.* 1047 (1979b).  
 Kawai, T. and Sakata, T., *Nature* **282**, 283 (1979a).  
 Maruska, H. P. and Ghosh, A. K., *Solar Energy* **20**, 463 (1976).  
 Sato, S. and White, J. M., *Chem. Phys. Lett.* **70**, 131 (1980a).  
 Sato, S. and White, J. M. (1980b) to be published.  
 White, J. M., Ph.D. Thesis, University of Illinois (1966).

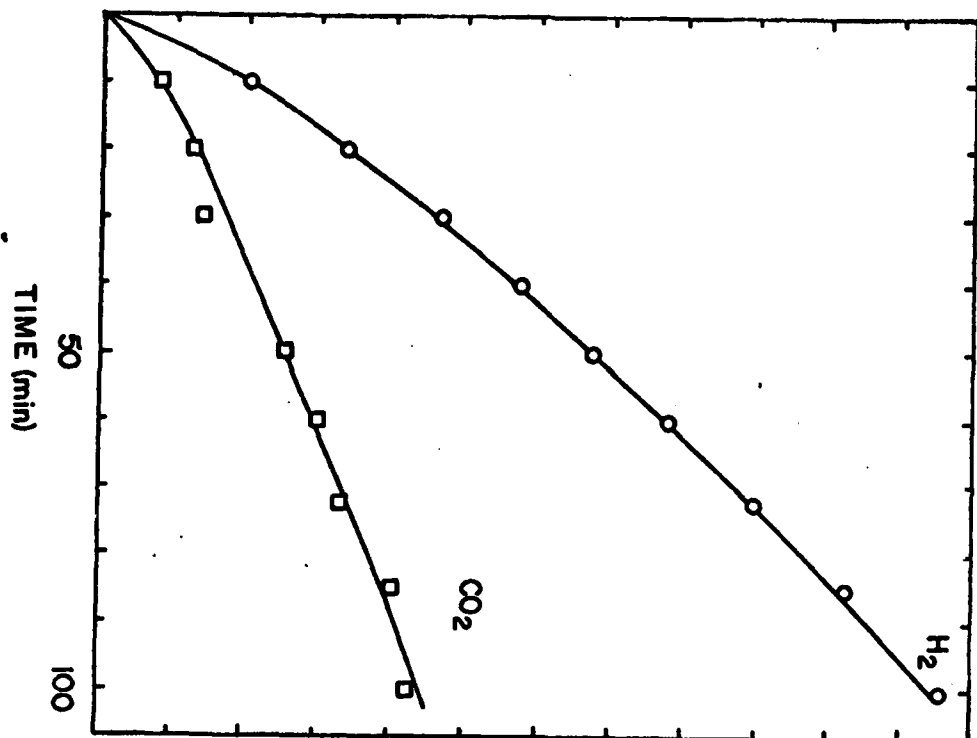
# Figure Captions

## Figure 1

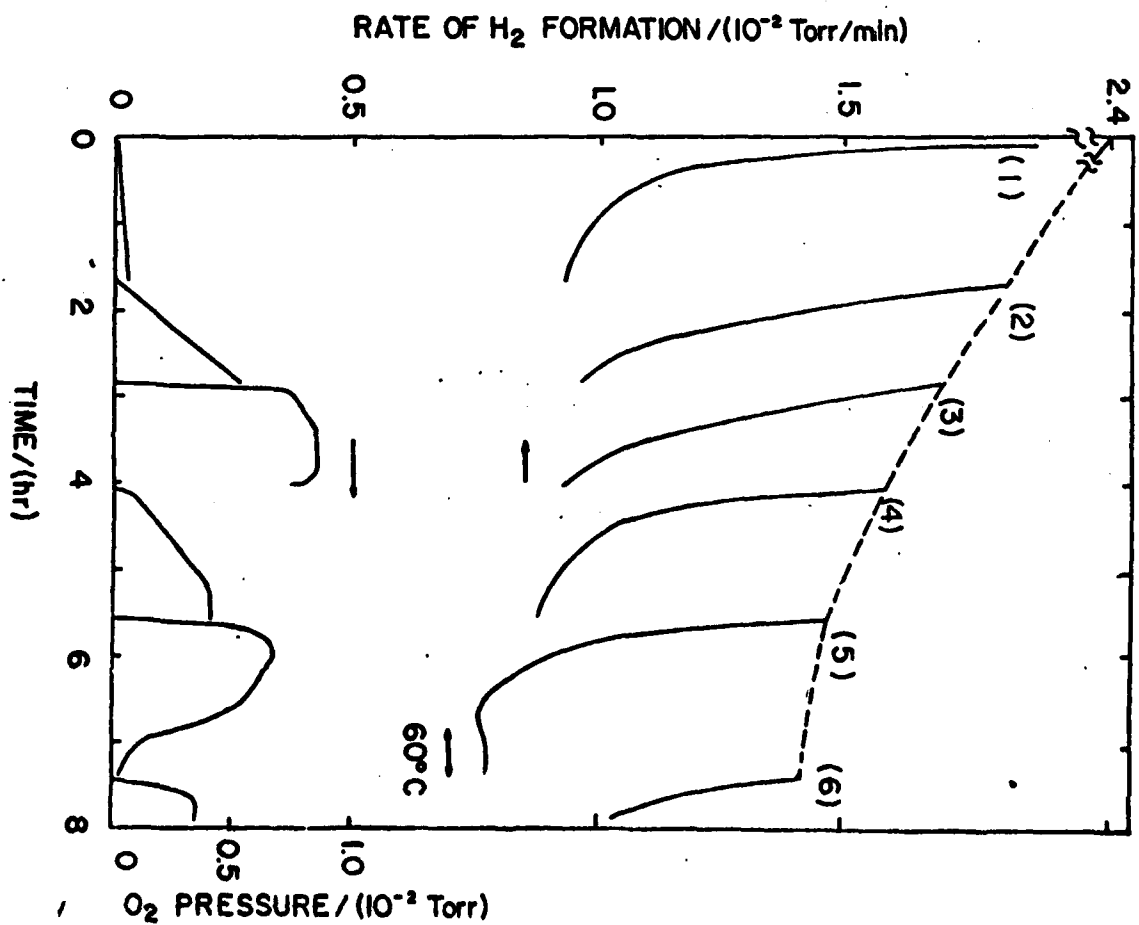
Photocatalytic production of  $H_2$  and  $CO_2$  from gaseous  $H_2O$  and Texas lignite by  $Pt/TiO_2$ .

## Figure 2

Changes in the rate of  $H_2$  formation (upper) and the pressure of  $O_2$  (below) during the reaction of Texas lignite with gaseous  $H_2O$  over UV-illuminated  $Pt/TiO_2$ . The products were evacuated at  $23^\circ C$  for 10 minutes before each run except runs 1 and 4, in which cases evacuation was at  $200^\circ C$  for 3 hr. Notice that in run 5, there is a segment during which the temperature was  $60^\circ C$ . The  $H_2$  production rates are scaled on the left-hand ordinate while the oxygen pressures are on the right.



Sub and units, Fig. 2



Sub and units, Fig. 2

**DA  
FILM**